Understanding the Nature of Marine Aerosols and Their Effects in the Coupled Ocean-Atmosphere System

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LONG-TERM GOALS

The long-term goal of this work is to understand the sources and nature of marine aerosol particles and how they influence visibility, cloud properties, the thermodynamic structure of the marine boundary layer, and the transmission of radiation.

OBJECTIVES

The objectives of this project extend across three areas: (i) advancing aerosol measurement techniques via the development of new instrumentation to quantify aerosol-water interactions and drop residual particle properties; (ii) improving knowledge and model predictions related to the physicochemical nature of aerosol particles and ocean-aerosol-cloud-precipitation-radiation interactions; and (iii) strengthening a research methodology leveraging multiple complementary tools of analysis to guide future studies of this nature in the marine atmosphere.

APPROACH

The main technical approach is to use a combination of in-situ aircraft measurements, cloud models, and satellite remote sensing data to study the nature and character of aerosols and their effects in the marine atmosphere over a broad range of spatial and temporal scales. The work during the last year included the following tasks:

- Data analysis of airborne and ship-board field data collected during an ONR-sponsored field experiment during the summer of 2011 called the Eastern Pacific Emitted Aerosol Cloud Experiment (E-PEACE)
- Joint analysis of satellite and model data to support science objectives during the E-PEACE field experiment, specifically rooted in aerosol-cloud-precipitation interactions
- Leadership and successful execution of an ONR-sponsored field experiment in the summer of 2013 called the Nucleation in California Experiment (NiCE), including data collection and organization for subsequent data analysis tasks in the upcoming year

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Key scientists involved with this work in the past year include Drs. Graham Feingold (National Oceanic and Atmospheric Administration) and Tristan L'Ecuyer (University of Wisconsin), who collaborated with the PI on using cloud models and interpreting satellite data to study cloud behavior in the marine atmosphere. The PI collaborated with Drs. Haflidi Jonsson (Naval Postgraduate School), John Seinfeld (California Institute of Technology), Bruce Albrecht (University of Miami), Lynn Russell (UC-San Diego), and Athanasios Nenes (Georgia Tech) to cooperatively analyze data collected during the 2011 E-PEACE study. The PI collaborated with Drs. Seinfeld and Jonsson for the successful execution of the NiCE airborne field experiment. An on-going collaboration with Dr. Daniel Partridge (University of Oxford) has involved conducting inverse modelling of aerosol-cloud interactions jointly with the use of airborne data for aerosol and cloud parameters in the marine atmosphere. Dr. Barbara Ervens (NOAA) collaborated with the PI in a project involving box model calculations of chemical processes occuring in marine stratocumulus cloud water.

WORK COMPLETED

Technical accomplishments in the previous year, include the following:

- Chemical characterization of cloud water samples collected during the E-PEACE field campaign and data analysis leading to a peer-reviewed manuscript with two more in preparation
- Analysis of aerosol and meteorological data collected on the Research Vessel Point Sur during the E-PEACE field campaign, leading to a peer-reviewed manuscript
- Analysis of satellite data leading to a peer-reviewed manuscript that describes and explores a novel method to estimate rates by which cloud water is converted to rain water in warm maritime clouds
- Analysis of data from multiple types of cloud models to advance understanding of the precipitation susceptibility of clouds to aerosol perturbations, leading to a peer-reviewed manuscript
- Successful execution of the 2013 NiCE field experiment with the CIRPAS Twin Otter

RESULTS

Results are divided below to coincide with separate peer-reviewed publications produced in the past year through research funded by this ONR YIP grant.

Investigation 1 (Sorooshian et al., 2013a):
This work examined organic acid and metal concentrations in northeastern Pacific Ocean stratocumulus cloud water samples collected by the CIRPAS Twin Otter between July and August 2011 during the E-PEACE field campaign. Organic acids are a critical chemical component of aerosol particles and cloud drops in the marine atmosphere, but their currently are gaps in knowledge about their production mechansims and sinks. Correlations between a suite of various monocarboxylic and dicarboxylic acid concentrations in cloud water during E-PEACE have provided insight into aqueous-phase mechanistic relationships leading up to oxalate production. Monocarboxylic and dicarboxylic acids exhibited contrasting spatial profiles reflecting their different sources; the former were higher in concentration near the continent due to fresh organic emissions. Concentrations of sea salt crustal tracer species, oxalate, and malonate were positively correlated with low-level wind speed suggesting that an important route for oxalate and malonate entry in cloud water is via some combination of

association with coarse particles and gaseous precursors emitted from the ocean surface. Three case flights show that oxalate (and no other organic acid) concentrations drop by nearly an order of magnitude relative to samples in the same vicinity (Figure 1). A consistent feature in these cases was an inverse relationship between oxalate and several metals (Fe, Mn, K, Na, Mg, Ca), especially Fe. By means of box model studies we showed that the loss of oxalate due to the photolysis of iron oxalato complexes is likely a significant oxalate sink in the study region due to the ubiquity of oxalate precursors, clouds, and metal emissions from ships, the ocean, and continental sources (Figure 2). The observation of an inverse relationship between metal and oxalate concentrations has major implications for predictive capabilities of oxalate formation in the atmosphere in light of recent modeling studies neglecting this sink (Myriokefalitakis et a., 2011). The E-PEACE measurements, together with box model simulations, can explain the significant overestimate of predicted oxalate levels versus in-cloud measurements in the same study region almost a decade ago (Crahan et al., 2004). It is further noted that this work has provided the first airborne in-cloud evidence of oxalate destruction by metals.

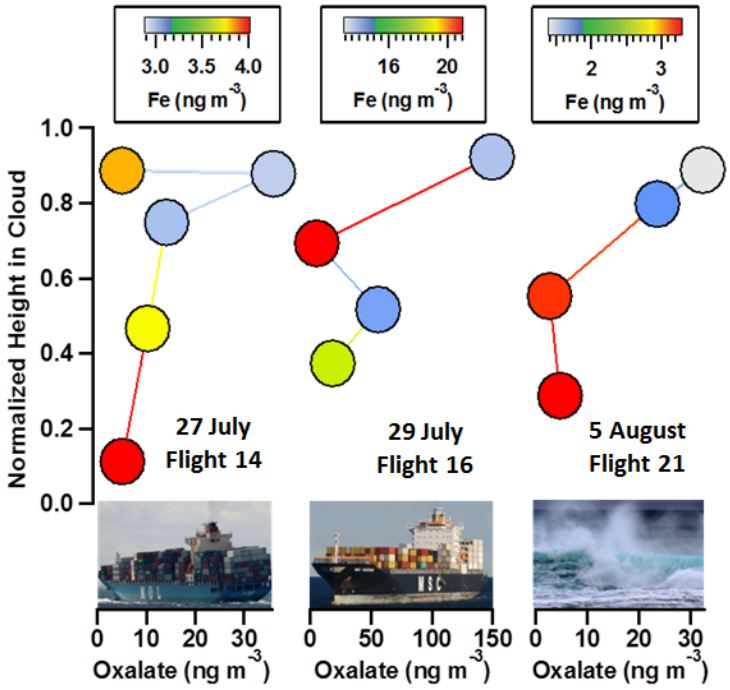

Figure 1. Vertically-resolved cloud water concentrations of oxalate and iron during three case flights in the 2011 E-PEACE field campaign. Normalized cloud heights of 0 and 1 correspond to cloud base and cloud top, respectively. The first two flights were impacted by ship emissions while the third one to the right was impacted more strongly by marine-derived sea spray emissions with minimal ship influence. Samples with enhanced iron during specific E-PEACE flights coincided with the lowest oxalate concentrations.

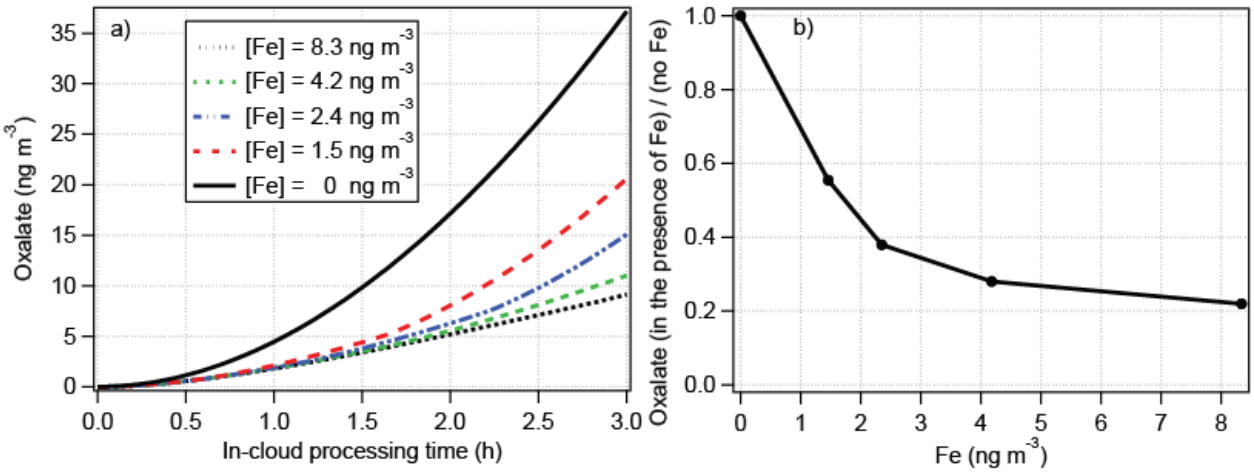

Figure 2. (a) Predicted oxalate concentrations as a function of cloud-processing time for different concentrations of total dissolved iron. (b) Ratio of predicted oxalate concentrations from simulations with and without iron as a function of total iron concentration dissolved in cloud water.

Investigation 2 (Wonaschütz et al., 2013):

During the E-PEACE field experiment, a plume of organic aerosol was produced by a smoke generator and emitted into the marine atmosphere from aboard the research vessel (R/V) *Point Sur* (Figure 3). A snapshot of the types of measurements conducted during the cruise is provided in Figure 4. We examined the hygroscopic properties and the chemical composition of the plume at plume ages between 0 and 4 hours in different meteorological conditions. In sunny conditions, the plume particles had very low hygroscopic growth factors (GFs = ratio of wet particle diameter to dry particle diameter): between 1.05 and 1.09 for 30 nm and 1.02 - 1.1 for 150 nm dry size at a relative humidity (RH) of 92%, contrasted by an average marine background GF of 1.6. New particles were produced in large quantities (several 10,000 cm^{-3}), which lead to substantially increased cloud condensation nuclei (CCN) concentrations at supersaturations between 0.07 – 0.88%. Ratios of oxygen to carbon (O:C) and water-soluble organic mass (WSOM) increased with plume age: from <0.001 to 0.2, and from 2.42 to 4.96 µg m^{-3}, respectively, while organic mass fractions decreased slightly (~0.97 to ~0.94). High-resolution aerosol mass spectrometer (AMS) spectra show that the organic fragment m/z 43 was dominated by $C_2H_3O^+$ in the small, new particle mode and by $C_3H_7^+$ in the large particle mode. In the marine background aerosol, GFs for 150 nm particles at 40% RH were found to be enhanced at higher organic mass fractions: an average GF of 1.06 was observed for aerosols with an organic mass fraction of 0.53, a GF of 1.04 for an organic mass fraction of 0.35.

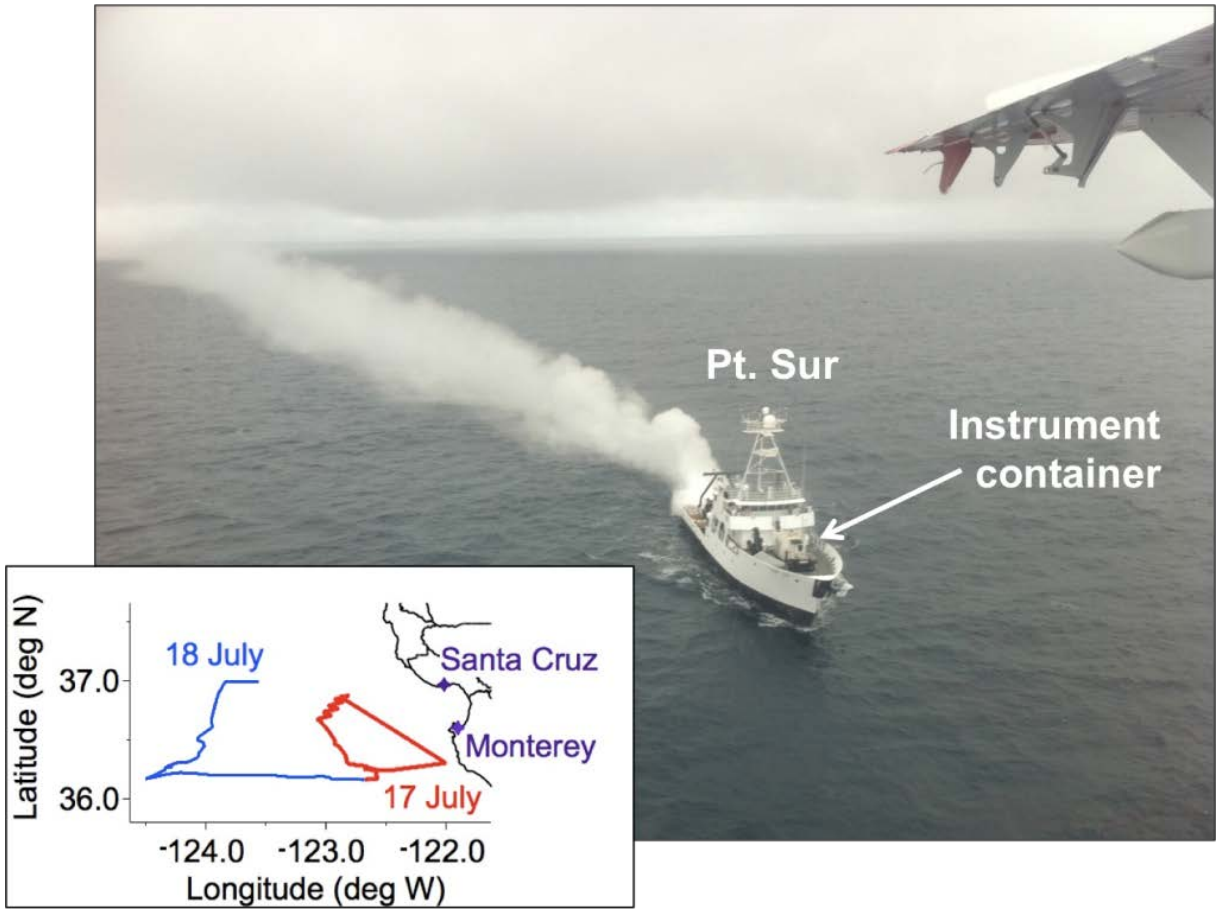

Figure 3. Smoke generation on the R/V Point Sur (photo taken from CIRPAS Twin Otter). Insert: General area of the E-PEACE field campaign off the coast of California. The ship's track is shown for the days that were the specific focus of this study.

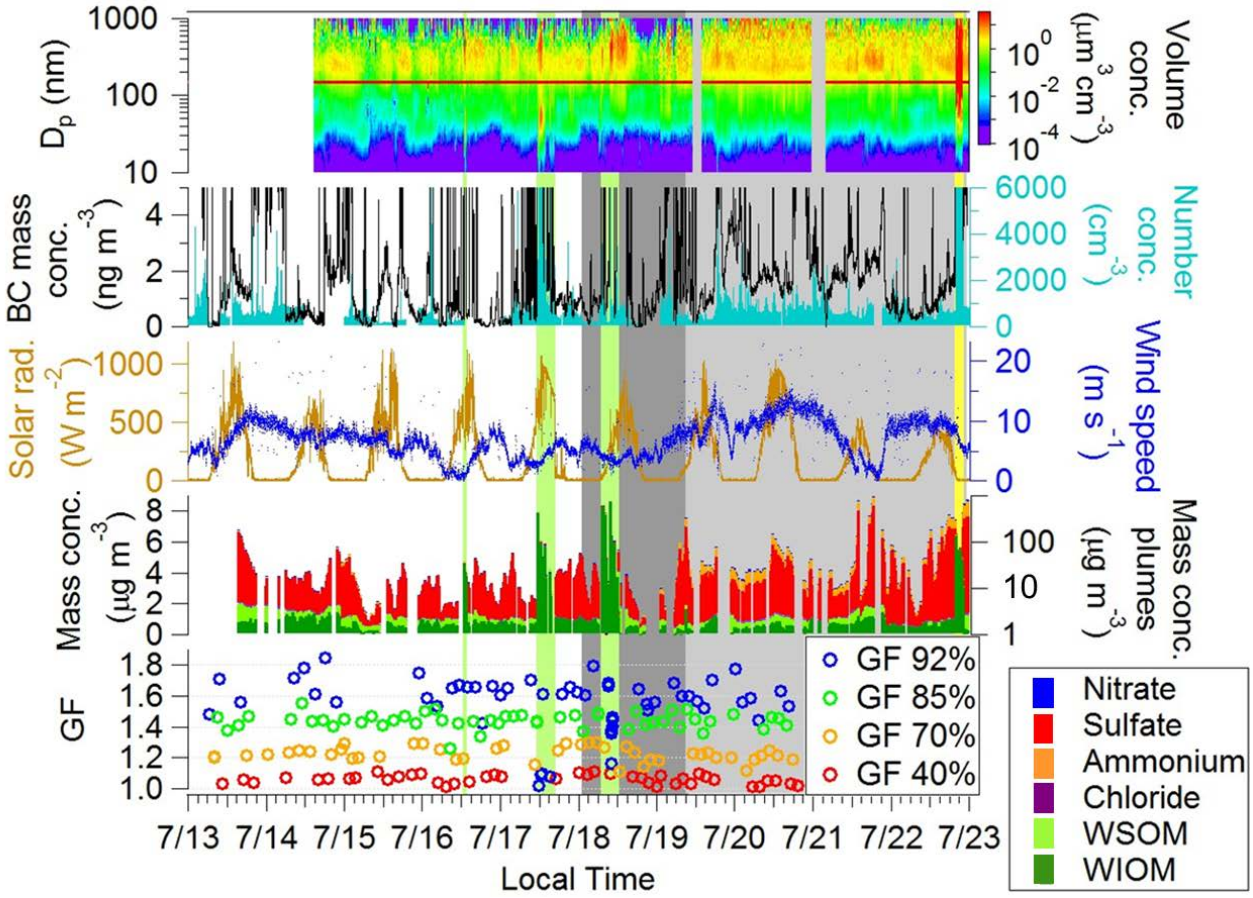

Figure 4. Sub-micrometer volume distributions (differential mobility analyzer, DMA), total number concentrations < 6000 cm^{-3} (condensation particle counter, CPC), black carbon concentrations < 5 ng m^{-3} (single particle soot photometer, SP2), chemical composition (aerosol mass spectrometer, AMS, and particle-into-liquid sampler, PILS, instruments) and hygroscopic growth factors (humidified tandem DMA, HTDMA) for a dry particle size of 150 nm (indicated in the volume distribution (top panel) by the red line) and four different RHs, as a function of time over the entire research cruise. Green shading corresponds to interception of the ship's own smoke plume, while yellow shading refers to interception of the ship's own stack exhaust. Mass concentrations for nitrate, sulfate, ammonium, chloride, water-soluble organic mass (WSOM), and water-insoluble organic mass (WIOM) in green or yellow shading (plumes) pertain to the right y-axis.

Investigation 3 (Sorooshian et al., 2013b):
A two-year satellite remote sensing dataset from the NASA A-Train was used to examine conversion rates of cloud water to rain water for warm maritime clouds with different ranges of mean cloud-layer radar reflectivity and rain rate. This work employs a novel procedure that relies on the differing sensitivities of passive MODIS measurements and active CloudSat radar measurements to estimate warm cloud conversion rates and associated time scales. That work is extended here to examine regional differences in conversion rates, including sensitivity to environmental parameters such as atmospheric stability and the presence of different aerosol types defined based on values of aerosol optical depth, fine mode fraction, and Ångstrom Exponent. Among eight sub-regions examined, the tropical Pacific Ocean is characterized by the highest average conversion rate while sub-tropical stratocumulus cloud regions (far northeastern Pacific Ocean, far southeastern Pacific Ocean, Western

Africa coastal region) exhibit the lowest rates (Figure 5). Conversion rates are generally higher at reduced values of lower tropospheric static stability (LTSS). When examining data in two selected ranges for LTSS, higher conversion rates are coincident with higher cloud liquid water path (LWP) and factors co-varying or rooted in the presence of aerosol types exhibiting lower aerosol index values, where aerosol index is considered as a proxy for columnar CCN concentrations.

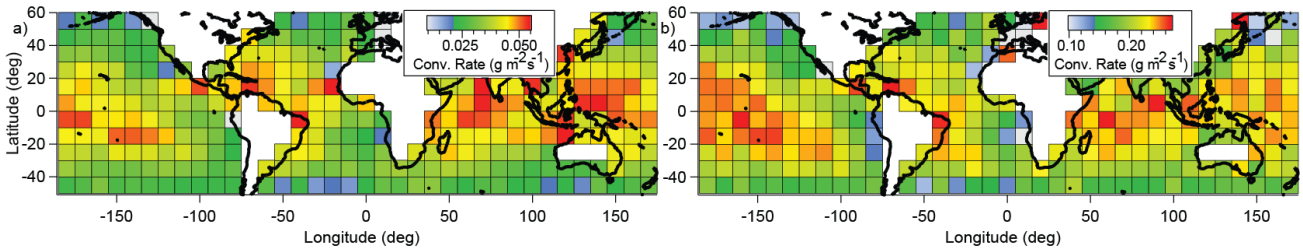

Figure 5. Spatial map of conversion rate of cloud water to rain water for data in two LWP bins: (a) ≤ 100 g m^{-2} and (b) ≥ 150 g m^{-2}. Sorooshian et al. (2013b) provide more details about various conditions used to filter data in order to construct these global maps.

Investigation 4 (Feingold et al., 2013):
The extent to which the rain rate from shallow, liquid-phase clouds is microphysically influenced by aerosol, and therefore drop concentration (N_d) perturbations, was addressed through analysis of the precipitation susceptibility, S_o ($= -\frac{d \ln R}{d \ln N_d}$, where R is precipitation rate). Previously published work, based on both models and observations, disagrees on the qualitative behavior of S_o with respect to variables such as liquid water path (LWP) or the ratio between accretion and autoconversion rates. Two primary responses have emerged in previous studies: (i) S_o decreases monotonically with increasing LWP and (ii) S_o increases with LWP, reaches a maximum, and decreases thereafter. This study used a variety of modeling frameworks ranging from box models of (size-resolved) collision-coalescence, to trajectory ensembles based on large eddy simulation to explore the role of time available for collision-coalescence t_c in determining the S_o response. The analysis shows that an increase in t_c shifts the balance of rain production from autoconversion (a N_d-dependent process) to accretion (roughly independent of N_d), all else (e.g., LWP) equal. Thus with increasing cloud contact time warm rain production becomes progressively less sensitive to aerosol, all else equal. When the time available for collision-coalescence is a limiting factor, S_o increases with increasing LWP whereas when there is ample time available, S_o decreases with increasing LWP. The analysis therefore explains the differences between extant studies in terms of an important precipitation-controlling parameter, namely the integrated liquid water history over the course of an air parcel's contact with a cloud.

IMPACT/APPLICATIONS

Results described in the previous section have direct connections to model parameterizations for treating aerosol microphysics and the interactions between particles and clouds.

RELATED PROJECTS

Related projects are sponsored by the National Science Foundation and NASA, which have provided support to assist with the PI's endeavor to use satellite data to investigate various aspects of aerosol-cloud interactions.

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